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METHOD FOR PREPARING PRE-REACTED BATCHES OF RAW MATERIALS FOR THE PRODUCTION OF GLASS FORMULAS

BACKGROUND OF THE INVENTION

A. FIELD OF THE INVENTION

This invention relates to batches of raw materials for preparing glass and more specifically to a method for preparing pre reacted batches of raw materials for the production of glass formulas, to which were added cullet (bits of recycling glass) to increase the velocity of the calcination process, the decarbonization grade of the batch and the formation of the desirable cristaline structures.

B. DESCRIPTION OF THE RELATED ART.

The batches for preparing molten glass have been provided, since many years, by feeding independent glass components typically silica, sodium carbonate, calcium carbonate, borates, feldspar, dolomite, kaolin, etc., in proportions according to a desired glass formulation, to a melting furnace at temperatures ranging between 1400 to 1600° C.

These typical batches include raw materials having different melting points and reacting at different temperatures under different operating conditions.

During the melting process of the raw materials, many different reactions take place in the glass melting furnace, which producing gaseous emissions in the form of bubbles which create the need for establishing a refining and conditioning zone for the molten glass mass in the furnace which, in turn, results in a limitation of the residence time of the molten mass, resulting in high

melting temperatures and the need to carefully control environmental emission restrictions.

Additionally, because of the high temperatures and corrosive nature of the diverse types of reactions taking place in the melting furnace, the life of the melting furnace is always an important issue.

The U.S. Pat. No 3,082,102 issued to Cole et al, discloses a process for producing molten glass by maintaining the glass batch at a temperature and for a time sufficient to complete chemical reaction between component particles while the batch as a whole remains in solid state at the completion of the reaction, before subjecting the embryo glass so formed to a temperature high enough to melt the embryo glass.

The U.S. Pat. No 4,920,080 issued to Demarsest, discloses a method for pre-heating and pre-reacting all portions of the batch prior to the melting step, in two separate portions, a first portion of SiO_2 with Na_2CO_3 in a first pre-reaction zone at sufficient time and temperature to form a product consisting predominantly of sodium silicate, and heating a second portion of SiO_2 with $CaCO_3$ in a second pre-reaction zone at sufficient time and temperature to render the calcium source free of carbonates.

It can be concluded from the methods disclosed in the above mentioned patents that efforts have been made to provide pre-reacted raw materials in which gaseous compounds have advantageously been eliminated.

However, the above disclosed methods treat all the batch mixtures at temperatures finely controlled to avoid that the reactions taking place do not

form a liquid melting phase because of the danger representing the difficulty of handling a batch including solid and liquid phases.

In the US Patent No. 6358870 issued to Antonio Pita and Hugo Bolio, and its corresponding Mexican patent application No. NL/a/2001/000043, is mentioned that a batch for the different purposes, mainly for flat glass, container glass (soda-lime and boro-silicate glass), glass fiber, etc., consists of a molecular formula comprising a diverse number of molecules of Si, Na, Ca, Mg, Bo, etc., which can be clearly approximated from natural, substances, partially treated minerals or intermediate products of treated minerals, including molecular systems of Si-Na, Si-Na-Ca, Si-Na-Mg, Si-Ca-Mg, Si-Na-Ca-Mg and mixtures thereof, some of which are in the form of already pre-reacted substances and some of which have to be conveniently pre-reacted in a calcining burner and, in either case, they are substantially free from gaseous carbon dioxide.

Also is described that, if phase diagrams are prepared for the different molecular systems of raw materials, it is possible to select molecular formulas having decomposing and/or melting temperatures well above at least 1000 °C, below which not only melting glass or liquid phase is not formed, but also the release of carbon dioxide can be clearly carried out, which are selected from invariant points or from points on a line connecting invariant points of phase diagrams of said molecular systems, and combine them to reach or approach the desired molecular glass formula, completing this by adding pure silica when necessary.

Also is commented that some of the mentioned of the phase diagrams of the above disclosed nature can be found for example in the papers of K. A. Shahid & F. P. Glosser "Phase equilibrium in the glass forming region of the system Na_2O-CaO-MgO-SiO_2" published in Physics and Chemistry of Glasses Vol. 13 No. 2 April 1972; and of G. W. Morey and N. L. Bowen, "Corner of system Na_2O-CaO-SiO_2" published by the Soc. Glass Technol., 9pp. 232, 233 (1925).

Said patent comment that, the those that it is looked for, is to saturate the sodium, calcium and in general all the elements of a glass formula that are handled with raw materials containing CO_2, to provide the specific molecular glass formula or at least a best approach of the molecular formula, completing the balance by providing silica sand

In this way, it is possible to provide a pre-reacted batch of raw materials for a specific molecular glass formula which:

1. Is greatly stable;

2. Melts faster and better;

3. Does not produce any bubbles due to the decomposition of the CO_2 components contained in the traditionally used raw material;

4. Reacts or melts at above 1000°C.

5. Is prepared by heating typical raw materials and reacting them as a solid-solid mixture which is de-carbonated between 840°C. and 870°C:

6. Allows the possibility of improving the glass quality and/or increasing the production rate and or reducing thermal input as well as reducing

temperature conditions in the furnace.

7. Allows the possibility of reducing environmental emissions.

8. Allows the possibility of increasing furnace life and/or reducing the size of the furnace for previously equal throughputs.

The inventor of the present invention have now found that, if cullet is added in the formulation, in bulk form or forming binders, the following advantages were surprisingly found:

1. The velocity of the calcination process is surprisingly increased.
2. The decarbonization grade of the mixture is increased to the double, that when cullet is not being used.
3. A significative impact in the formation of the desirable cristaline structures is presented, since that its use, permits the formation of, in a great part of, calcium and sodium silicate ($Na_2CaSi_3O_9$).

The advantages above cited were tested by means of "X" rays diffraction analysis, which were realized on test samples that were carried out in three campaigns.

The mechanism through which the cullet permits the improvements above mentioned, in the process, is not of all known, but this could be explained due to that a better heat transfer of the cullet toward the reactives that are agglomerated in the briquettes that is being formed with the formulations, which allows a better heat diffusion, permitting the formation of the searched species, accelerating the solid-solid reaction.

SUMMARY OF THE INVENTION

It is therefore a main object of the present invention, to provide a new method for preparing pre-reacted batches of raw materials for the production of glass formulas, which comprises to add cullet, before to be subjected to calcinations, to stoichiometric amounts of substances containing molecular systems of silica-sodium, silica-sodium-calcium, silica-sodium-magnesium, silica-calcium-magnesium, silica-sodium-calcium-magnesium and mixtures thereof having reaction temperatures which do not form a liquid phase, which are selected from invariant points or from points on a line connecting invariant points of phase diagrams of said molecular systems, to complete or approach a desired molecular glass formula.

It is also a main object of the present invention, to provide a method for preparing pre-reacted batches of raw materials for the production of glass formulas, of the above disclosed nature, which add cullet to the batches before to be subjected to a calcinations process, increasing surprisingly the velocity of the calcination process,

It is still a main object of the present invention, to provide a method for preparing pre-reacted batches of raw materials for the production of glass formulas, of the above disclosed nature, in which, when the cullet is added to the batches, before to be subjected to calcination, the decarbonization grade of the mixture is increased to the double, that when cullet is not being used.

It is a further main object of the present invention, to provide a method

for preparing pre-reacted batches of raw materials for the production of glass formulas, of the above disclosed nature, in which, by the adding of selected amounts of cullet, before to be subjected to calcination, a significative impact in the formation of the desirable cristaline structures is presented, since that its use, permits the formation of, in a great part of, calcium and sodium silicate.

These and other objects and advantages of the method for preparing pre-reacted batches of raw materials for the production of glass formulas, of the present invention will become apparent from the following detailed description of the invention, provided as specific embodiments thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

The figures 1 through 8 are diagrams of the residence time against the kiln temperature and the CO_2 content of the test carried out with the following molecular systems: Na-Ca-5Si; Na-Ca-5Si (foundry silica); Na-Mg-4Si; Na-Mg-4Si (foundry silica); Na-3Ca-6Si; Na-3Ca-6Si (foundry silica); Na-3Ca-6Si (foundry silica); and Na-2Ca-3Si.

DETAILED DESCRIPTION OF THE INVENTION

In its most general aspect, the method for preparing pre-reacted batches of raw materials for the production of glass formulas, comprising:

mixing stoichiometric amounts of substances selected from natural minerals, partially treated minerals or intermediate products therefrom containing molecular systems of silica-sodium, silica-sodium-calcium, silica-sodium-magnesium, silica-calcium-magnesium, silica-sodium-calcium-magnesium and mixtures thereof having reaction and CO_2 release

temperatures under 1000°C, which do not form a liquid phase at such temperatures, which were selected from invariant points or from points on a line connecting invariant points of phase diagrams of said molecular systems, to complete or approach to a desired molecular glass formula;

adding selected amounts of cullet to the batch;

calcining the batch to obtain the pre-reacted batches of raw materials for use in glass formulas.

For convenience, the mixture that was prepared with the adding cullet is subjected to agglomeration to form briquettes, which are subjected at a later time to a calcination process.

The selection of the molecular systems from invariant points in the phase diagrams were taken on the basis of the desired molecular glass formula as follows:

1. Molecular System Si-Na:	SiNa
2. Molecular System Si-Na-Ca:	$Si_3Na_2Ca_2$ Si_3NaCa_2 Si_6NaCa_3 Si_5NaCa
3. Molecular System Si-Na-Mg	$Si_{12}NaMg_5$ Si_6NaMg_2 Si_4NaMg Si_6NaMg

For a molecular flat glass formula comprising $Si_{73}Na_{15}Ca_9Mg_4$, the molecular systems selected were:

$4(Si_4NaMg)$ = 16Si- 4Na-4Mg;	$4(Si_6NaMg)$ = 24Si-4Na-4Mg
$3(Si_6NaCa_3)$ = 18Si- 3Na-9Ca	$3(Si_6NaCa_3)$= 18Si- 3Na-9Ca

$$8(SiNa) = \frac{8Si - 8Na}{42Si\text{-}15Na\text{-}4Mg\text{-}9Ca} \qquad 8(SiNa) = \frac{8Si - 8Na}{54Si\text{-}15Na\text{-}4Mg\text{-}9Ca}$$

$$\text{The balance } \frac{31Si}{73Si\text{-}15Na\text{-}4Mg\text{-}9Ca} \qquad \text{The balance } \frac{19Si}{73Si\text{-}15Na\text{-}4Mg\text{-}9Ca}$$

For a molecular silica-lime glass container formula comprising Si_{73} Na_{15} Ca_6, the molecular systems selected were:

$$3(Si_6NaCa_3) = 18Si\text{- }3Na\text{-}9Ca \qquad 9(Si_5NaCa) = 45Si\text{- }9Na\text{-}9Ca$$

$$12(SiNa) = \frac{12Si\text{-}12Na}{30Si\text{-}15Na\text{-}9Ca} \qquad 6(SiNa) = \frac{6Si\text{- }6Na}{51Si\text{-}15Na\text{-}9Ca}$$

$$\text{The balance } \frac{43Si}{73Si\text{-}15Na\text{-}9Ca} \qquad \text{The balance } \frac{22Si}{73Si\text{-}15Na\text{-}9Ca}$$

For the selection of the desired molecular systems, firstly Differential Test Analysis (DTA) and Thermal Gravimetric Analysis were carried out in order to verify that the de-carbonating temperature and the fact that the reaction temperature of the total selected batch were under the melting temperature.

In a second step, tests were conducted in a batch calcining kiln in which 10 different compounds were processed, extracting samples of each compound every 5 minutes analyzing the CO_2 content of half of the samples and analyzing the characteristic of the other half of the samples by means of an X ray diffraction apparatus and, from the results, the three most important compounds for the glass formulations were selected.

In a third step, tests were conducted in a pilot calcining kiln, producing 2 tons of pre-decomposed and pre-reacted compounds during 48 hours, extracting samples each 30 minutes, analizing the CO_2 content of a half of the samples and analyzing the characteristics of the other half of samples by means of an X ray diffraction apparatus.

An last but not least, in a fourth step, industrial tests were carried out by producing 850 tons of a soda-lime-magnesium compounds in an industrial rotary kiln mixing it with the balancing raw materials required to form a glass batch formula and introducing the same in a 110 tons per day glass furnace without increasing the production rate, the following results were obtained during a test that run continuously for 11 days:

	TYPICAL	INVENTION	DIFFERENCE
THERMS	92	77	15
CROWN TEMPERATURE	1470°C	1420°C	50°C
GLASS TEMPERATURE (AT THE FURNACE EXIT)	1170 °C	1105°C	65°C
PARTICLE EMISSION (Kg/Ton)	0.04	0.0	0.04
NOx (Kg/Ton)	7.12	3.72	3.40

The furnace life was estimated to increase at least one year.

The specific Examples for tests of the second step, extracting samples of each compound every 5 minutes analyzing the CO_2 content in the diverse molecular systems for molecular glass formulations, which were respectively plotted in the diagrams of FIGS. 1 to 8, where:

EXAMPLE 1

For a molecular system comprising Na--Ca--5Si three samples were extracted and analyzed, obtaining the following results illustrated in FIG. 1:

Sample #	Min.	Initial lecture	Final Lecture	Inictial-Final	Factor	% $CaCO_3$	Factor	% CO_2
2	5	94.4	48.2	46.2	1.1	50.82	0.43	21.85
4	15	53.4	34.6	18.8	1.1	20.68	0.43	8.89
6	25	56.8	44.2	12.6	1.1	13.86	0.43	5.96

EXAMPLE 2

For a molecular system comprising Na--Ca--5Si (foundry silica), four samples were extracted and analyzed, obtaining the following results, illustrated in FIG. 2:

Sample #	Min.	Initial Lecture	Final Lecture	Initial-Final	Factor	% $CaCO_3$	Factor	% CO_2
2	5	61.2	42.0	19.2	1.1	21.12	0.43	9.08
4	15	56.4	47.4	9.0	1.1	9.90	0.43	4.26
6	25	46.0	43.2	2.8	1.1	3.08	0.43	1.32
8	35	46.0	43.8	2.2	1.1	2.42	0.43	1.04

EXAMPLE 3

For a molecular system comprising Na--Mg--4Si, seven samples were extracted and analyzed, obtaining the following results, illustrated in FIG. 3:

Sample #	Min.	Initial Lecture	Final Lecturel	Initial-Final	Factor	% $CaCO_3$	Factor	% CO_2
1	0	52.6	41.8	10.8	1.1	11.88	0.43	5.11
2	5	44.8	41.6	3.2	1.1	3.52	0.43	1.51
3	10	37.8	35.0	2.8	1.1	3.08	0.43	1.32
4	15	44.6	41.6	3.0	1.1	3.30	0.43	1.42
5	20	45.6	42.2	3.4	1.1	3.74	0.43	1.61
6	25	32.4	31.4	1.0	1.1	1.10	0.43	0.47
7	30	47.4	45.4	2.0	1.1	2.20	0.43	0.95

EXAMPLE 4

For a molecular system comprising Na-Mg-4Si (foundry silica), nine samples were extracted and analyzed, obtaining the following results illustrated in FIG. 4.

Muestra #	Min.	Lectura Inicial	Lectura Final	Inicial-Final	Factor	% $CaCO_3$	Factor	% CO_2
1	0	57.8	42.8	15.00	1.1	16.50	0.43	7.10
2	5	64.0	44.0	20.00	1.1	22.00	0.43	9.46
3	10	56.4	45.8	10.60	1.1	11.66	0.43	5.01
4	15	51.8	45.2	6.60	1.1	7.26	0.43	3.12
5	20	45.4	43.2	2.20	1.1	2.42	0.43	1.04
6	25	41.8	37.8	4.00	1.1	4.40	0.43	1.89
7	30	45.8	3.40	3.40	1.1	3.74	0.43	1.61
8	35	46.0	3.24	3.20	1.1	3.52	0.43	1.51
9	40	36.8	436.4	4.00	1.1	4.40	0.43	1.89

EXAMPLE 5

For a molecular system comprising Na-3Ca-6Si, nine samples were extracted and analyzed, obtaining the following results, illustrated in FIG. 5:

Sample #	Min.	Initial Lecture	Final Lecture	Initial-Final	Factor	% $CaCO_3$	Factor	% CO_2
1	5	52.4	42.4	10.0	1.1	11.00	0.43	4.73
2	10	42.2	35.6	6.6	1.1	7.26	0.43	3.12
3	15	48.8	46.0	2.8	1.1	3.08	0.43	1.32
4	20	44.6	42.4	2.2	1.1	2.42	0.43	1.04
5	25	45.6	43.6	2.0	1.1	2.20	0.43	0.95
6	30	41.8	39.8	2.0	1.1	2.20	0.43	0.95
7	35	37.6	36.0	1.6	1.1	1.76	0.43	0.76
8	40	47.6	45.4	2.2	1.1	2.42	0.43	1.04
9	45	42.4	40.4	2.0	1.1	2.20	0.43	0.95

EXAMPLE 6

For a molecular system comprising Na-3Ca-6Si (foundry silica), eleven samples were extracted and analyzed, obtaining the following results, illustrated in FIG. 6:

Sample #	Min.	Initial Lecture	Final Lecture	Initial-Final	Factor	% $CaCO_3$	Factor	% CO_2
1	0	94.0	41.2	52.8	1.1	50.8	0.43	24.97
2	5	72.6	36.4	36.2	1.1	39.82	0.43	17.12
3	10	62.2	39.8	22.4	1.1	24.64	0.43	10.60
4	15	49.8	40.4	9.4	1.1	10.34	0.43	4.45
5	20	44.8	39.0	5.8	1.1	6.38	0.43	2.74
6	25	45.0	40.4	4.6	1.1	5.06	0.43	2.18
7	30	45.2	40.6	4.6	1.1	5.06	0.43	2.18
8	35	49.0	44.8	4.2	1.1	4.62	0.43	1.99
9	40	47.6	43.0	4.6	1.1	5.08	0.43	2.18
10	45	46.6	43.0	3.6	1.1	3.96	0.43	1.70
11	50	46.0	42.6	3.4	1.1	3.74	0.43	1.61

EXAMPLES 7 and 8

Finally, for molecular systems comprising Na-3Ca-6Si (foundry silica) and Na-2Ca-3Si, eleven and eight samples were extracted and analyzed, obtaining the results illustrated in FIGS. 7 and 8.

To confirm the effects of adding cullet to the mixture of raw materials for preparing the pre-reacted batches, three experimentation campaigns forming briquettes of raw materials, were carried out. The first ant the third without the addition of cullet and the second, in the experiment 8 and 9, for a formulation containing three parts of SiO_2, two parts of Na_2O, and one part of CaO, as well as, adding a small amount of a formulation containing three parts of SiO_2, one part of Na_2O and two parts of CaO (which are identified as 3:2:1 + 3:1:2). In this formulation a 20% by weight of cullet was approximately added, obtaining the following results:

Table 1

Time to Temperature	Experiment 8		Experiment 9		Experiment 10		Experiment 11	
	Temp °C	CO_2%	Temp °C	CO_2%	Temp °C	CO_2%	Temp °C	CO_2%
75	877	0.75	875	0.55	875	5.86	877	3.24
90	885	0.78	875	0.75	879	2.75	885	2.64
105	893	0.61			875	3.26	876	1.66
120	8.73	0.61			879	2.55	874	1.12

Table 2

Chemical and mineral analysis of the glass formula 5.1.1. Campaign 1.

Experiment No. Run of Briquette No.	Name of PDF#	Angle 2- Teta	1 1	2 1	3 2
SiO_2, % Quartz	33-1161	26.6°	~25-35%	~25-35%	~25-35%
$Na_4CaSi_3O_9$	37-0282	48.2°	Traces	Traces	Traces
$Na_2Ca_2Si_2O_7$	10-0016	33.0°, 49.6°	Traces	Traces	Traces
$Na_2CaSi_3O_8$	12-0671	48.6°	Minor	Subord.	Minor
CaO Cal	37-1497	37.3°, 53.9°	Traces-minor	Traces-minor	Traces-minor

The Categories are Major, Subordinate (Subord) Minor, Traces and No detected (ND). The enunciate on the row provides the formula, name or PDF and Number and the Angle 2-Teta of the peak that was measured.

Table 3

Chemical and mineral analysis of the glass formula 3.2.1 + 3.1.2 Campaign 2

Experiment No. Run of Briquette No.	Name of PDF#	Angle 2- Teta	8 1	9 1	10 1
SiO_2, % Cuarzo	33-1161	26.6	~1.3%	~2.0%	~5.0%
$Na_4CaSi_3O_9$	37-0282	33.5°, 48.2°	Major	Major	Major
$Na_2Ca_2Si_2O_7$	10-0016	33.0°, 49.6°	Subord.	Subord.	Subord.
$CaCO_3$	05-0586	29.3°	Minor	Minor	Minor
Na_2CO_3	37-0451	30.2°	ND	ND	Traces
CaO Cal	37-0497	37.3°, 53.8°	ND	ND	ND
Amorphous glass			ND	ND	ND

Tabla 4

Chemical and mineral analysis of the glass formula 5.1.1 + 1.1 Campaign 3

Experiment No. Run of Briquette No.	Name of PDF#	Angle 2- Teta	16 Prod 2	17 Prod 2	18 Prod 4
SiO_2, % Quartz	33-1161	26.6	~28%	~34%	~35%
$Na_2CaSi_3O_9$	37-0282	33.5°, 48.2°	Minor	Minor	Minor
$Na_2Ca_2Si_2O_7$	10-0016	33.0°, 49.6°	Traces	Traces	Minor
$Na_2CaSi_3O_8$	12-0671	48.6°	Minor	Minor	Minor
$CaCO_3$	05-0586	29.3°	Traces	ND	Traces
Na_2CO_3	37-0451	30.2°	Minor	Traces	Traces
CaO Cal	37-1497	37.3°, 53.8°	ND	ND	Traces
Amorphous glass			ND	ND	ND

The results of the Table 1, shows the surprisingly benefic effect that the cullet has in the velocity of the calcination process, as well as, in the decarbonization grade of the mixture (remaining with a content of between 1 and 0.5% of CO_2), because permits the heat penetration within the briquette of the mixture of raw materials, that is absorbed toward the centre of the briquettes, giving as result a more complete reaction of the components of the mixture. Furthermore, in the experiments 8 and 9, the levels of carbon dioxide were maintained 1% per below of the limit.

These data carrying to the inventor to define the approximately performance limits of the amounts of cullet that is useful to add to the mixture of the raw materials, between un 5 y 25% by weight, and to be agglomerated before to be submitted to a calcination process.

Finally regarding to the formation grade of the desirable crystalline structures, the results of the campaign 3, for the campaign in that was used the cullet, in comparation with the results obtained in the tables 2 and 4, these shows the desirable formation of the crystalline structures $Na_4CaSi_3O_9$ y $Na_2Ca_2Si_2O_7$.